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<p>(21) International Application Number: PCT/EP93/01704</p> <p>(22) International Filing Date: 30 June 1993 (30.06.93)</p> <p>(30) Priority data: 92202112.6 10 July 1992 (10.07.92) EP</p> <p>(34) Countries for which the regional or international application was filed: NL et al.</p> <p>93200088.8 14 January 1993 (14.01.93) EP</p> <p>(34) Countries for which the regional or international application was filed: NL et al.</p> <p>(71) Applicant (for AU BB CA GB IE LK MN MW NZ SD only): UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4 4BQ (GB).</p>		<p>(71) Applicant (for all designated States except AU BB CA GB IE LK MN MW NZ SD): UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).</p> <p>(72) Inventors: BROCKHUS, Jeroen, Johannes, J., J. ; Neubourgstraat 14, NL-4834 JM Breda (NL). LAMMERS, Jannes, Gerrit ; Hohenkamp 1, D-2875 Ganderkesee 2 (DE). MOREE, Jeanette, Digna ; Mondlanestraat 10, NL-2807 RJ Gouda (NL). RODENBURG, Tileman ; Abeltasmanlaan 218, NL-3133 AD Vlaardingen (NL).</p> <p>(74) Agent: HARTONG, Richard, Leroy; Unilever N.V., Patent Division, P.O. Box 137, NL-3130 AC Vlaardingen (NL).</p> <p>(81) Designated States: AT, AU, BB, BG, BR, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published With international search report.</p>
<p>(54) Title: GLAZING AGENT</p> <p>(57) Abstract</p> <p>The invention concerns ready-to-use glazing agents with the composition: 1-25 wt.% of liquid oil; 5-15 wt.% of casein or its salts; 0.05-10 wt.% of emulsifier; 0.1-8.0 wt.% of a compound giving a browning, preferably by a Maillard-type of reaction; balance: water. The composition is sterilizable and has a shelf-life after sterilization of more than 3 months.</p>		

GLAZING AGENT

The invention is concerned with glazing agents that are ready to use.

5 Glazing agents that are not ready to use are known from, e.g., EP 205,195. According to this reference, a glazing agent can be provided comprising a homogenized emulsion of a protein, an edible oil, water and a thin-boiling starch. The thin-boiling starch is applied in order to regulate the viscosity of the emulsion.

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However, the keepability of such a glazing agent was not sufficient. Although this keepability could be increased by drying the glazing agent, the resulting product was no longer ready to use.

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Therefore, we have performed a study in order to find a glazing agent that :

- is ready to use;
- has the required spreadability, i.e. viscosity;
- 20 - shows good keepability.

As a result of this study, we have found that ready-to-use glazing agents fulfilling the above-mentioned requirements have the following composition :

25

They are fat-in-water emulsions comprising :

1-25 wt.%, preferably 5-15 wt.%, of a liquid vegetable oil;

5-15 wt.%, preferably 8-11 wt.%, of casein or one
30 of its salts;

0.005-10 wt.% of an emulsifier, preferably 0.01-1.0 wt.% of an emulsifier, in particular one selected from the group of fatty acid monoglycerides and diglycerides from C₁₄-C₂₂, preferably saturated and/or unsaturated C₁₆-
35 C₁₈ fatty acids;

0.1-8.0 wt.% of a composition giving a browning upon heating, preferably a Maillard-type reaction, such as lactose, or a milk product containing lactose, amounts of 0.3-3 wt.% being preferred, while suitable milk products are skimmed milk powder or buttermilk powder;
5 balance : water

The liquid vegetable oil being defined as an oil being liquid up to 30°C (so: $N_{30} \approx 0$). So, our composition is
10 free of starch or modified starch.

The viscosity of the composition at 20°C is $1-10^5$ mPa.s, preferably 20-200 mPa.s..

15 The keepability of these compositions is very satisfactory as the compositions can be sterilized by UHT treatment, i.e. 1-30 seconds at 130-160°C. After this treatment, the viscosity of the glazing agent remains within the specifications, while keepabilities (ambient shelf-lives)
20 are obtained for at least 3 months.

The best results are obtained by applying a liquid vegetable oil with a solid fat index at 20°C of less than 7.0, a preferred oil being a medium-hardened soybean oil.

25 This liquid oil can also comprise some amount, in particular 2-15 wt% on oil, of a hydrogenated vegetable fat. A preferred fat being hydrogenated palm oil, in particular PO-45. Application hereof improves the viscosity
30 and the stability of the product.

It was further found, that the desired colouring, due to heating of a food product provided with a layer of our glazing agents, could be obtained, when our compositions
35 contained 0.1-8.0 wt% of a compound or a mixture that can give a a browning upon heating, preferably by a Maillard-type of reaction. Browning can be obtained by Maillard

reactions (amino sugar reactions), by caramelization of sugars or by oxidative reactions. Examples of Maillard compositions are lactose, preferably in combination with a protein-source, such as milk products containing lactose.

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The stability of the water-continuous emulsion is greatly dependent on the droplet size of the fat droplets in the emulsion. Droplet sizes of less than 5.0 μm , in particular of 0.5-2.0 μm , are preferred.

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We also found that the presence of some egg-yolk in our composition leads to an improved emulsion stability. Therefore, we prefer that our ready-to-use glazing agents also comprise 1-10 wt% in particular 2-8 wt% of an egg-yolk composition. Preferred egg yolk compositions contain some salt, in particular 5-15 wt% (on egg yolk).

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The glazing agents according to the invention can be applied on normal dough (i.e. of ambient temperature) and on frozen dough. Baking of the dough, with or without thawing of the dough before baking, leads to excellent gloss, appearance and colour of the baked products.

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The glazing agent is normally applied in amounts of 30-100 mg/cm^2 . Spraying or atomizing are standard techniques for the distribution of the glazing agent; however, brushing should also be possible.

25

Although above products display excellent glazing properties, we found that upon use (by spraying) of the glazing agent over the product to be baked, which normally is performed on a baking-sheet, the part of the material, that is in direct contact with the hot baking-sheet is very difficult to remove from the baking sheet after baking of the product.

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In order to improve the cleaning abilities of our glazing

agents, we found that addition of 0.05-2.5 wt% of a pyrophosphate, in particular 0.1-1.5 wt%, resulted in the required improvement. Preferred pyrophosphates are the alkali-pyrophosphates, preferably sodium pyrophosphate.

5

Good results have been obtained by any of the following procedures :

- 10 I 1. making a dough, moulding and proofing it;
2. coating it with glazing agent;
3. baking of fresh product.
- 15 II 1. making a dough and moulding it;
2. coating it with glazing agent;
3. baking of fresh product.
- 20 III 1. making a dough, moulding and proofing it;
2. coating it with glazing agent;
3. freezing of the coated product;
4. frozen storage : 3 weeks;
5. baking of the frozen product without thawing.
- 25 IV 1. making a dough and moulding it;
2. coating of the dough with glazing agent;
3. freezing of the coated dough;
4. frozen storage : different periods;
5. thawing of the frozen, coated dough;
6. proofing of the product of 5);
7. baking of the product of 6).
- 30 V 1. making a dough and moulding it;
2. coating it with glazing agent;
3. freezing of the dough;
4. frozen storage : different periods;
35 5. thawing;
6. baking of the coated, thawed, frozen dough.

In process IV, relative humidity has an impact on the product properties. It was found that too high an R.H. (i.e. > 60%) led to relatively worse products.

- 5 It is also possible to apply the glazing agent according to the invention for the preparation of microwavable, proofed, baked, frozen and coated doughs.

EXAMPLES

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I A pre-mix was made in water of 80°C containing the water, skimmed milk powder and sodium caseinate.

15 Simultaneously, a mixture of unsaturated mono- and diglycerides was dissolved in soybean oil ($N_{20} \approx 0$).

The fat mixture was added to the water phase and the mixture was subjected to Ultra Turrax mixing for 5 minutes. The $D_{3,2}$ (= droplet size) was 3.8 μm .

20

The composition was sterilized by indirect heat treatment (8 seconds at 140°C).

The composition of the resulting glazing agent was :

25

	<u>wt. %</u>
Water	80.0
Na-caseinate	10.0
SMP	2.0
30 BO	7.9
Emulsifier	0.06

The viscosity (η_{20}) of the sterilized product was about 200 mPa.s.

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II The procedure of Example I was repeated; however, the Ultra Turrax mixing was followed by a pressure-

homogenization procedure (at about 50 bar). This resulted in a product having a droplet size before sterilization of about 1.9 μm . The η_{20} of the sterilized product was about 100 mPa.s.

5

III The products were evaluated on the following product types : Dänische Brötchen, croissants, puff pastry sheets and "gevulde koeken" (\approx almond paste cakes).

10 Therefore, the procedures mentioned above (I-V) were applied, as illustrated in Table I.

TABLE I

Procedure	P r o d u c t s			
	Yeast-leavened rich dough: 'Dänische Brötchen'	Yeast-leavened laminated dough: Croissants	Laminated dough: Puff pastry sheets	Short dough: 'gevulde koeken' (\approx almond paste cakes)
	S a m p l e n u m b e r			
I	1	2		
II			3	4
III Frozen storage: 3 weeks		5		
IV Frozen storage: 2 weeks 3 weeks 90% - RH 45% - RH	6 6	7/8 7 8		
V 2 weeks			9	10

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In Tables II and III a comparison is made between coatings obtained with the composition according to the invention, coatings obtained from whole egg and coatings obtained with a commercially available, not ready-to-use mix "Ovex bakglans" (ex Zeelandia).

'Dänische Brötchen'	Whole egg reference	OVEX bakglans	S a m p l e n u m b e r				
			1	2	3	4	5
Gloss remarks:	3	2	3				
Appearance remarks:	3	2	3				
Colour remarks:	3	3	3				
Mouthfeel crust remarks:	3	3	3.5				

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Croissants	Whole egg reference	OVEX bakglans	S a m p l e n u m b e r				
			1	2	3	4	5
Gloss remarks:	3			4			4
Appearance remarks:	3			4			4
Colour remarks:	3			3			3
Mouthfeel crust remarks:	3						

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TABLE II (cont.)

Puff pastry Sheets	Whole egg reference	OVEX bakglans	S a m p l e n u m b e r				
			1	2	3	4	5
Gloss remarks:	3	3			3		
Appearance remarks:	3	3			3		
Colour remarks:	3	3			3		
Mouthfeel remarks:	3	3.5			3.5		
'Gevulde Koecken' (\approx almond paste cakes)	Whole egg reference	OVEX bakglans	S a m p l e n u m b e r				
			1	2	3	4	5
Gloss remarks:	3	3				3	
Appearance remarks:	3	4				4	
Colour remarks:	3	4				4	
Mouthfeel remarks:	3	3				3	

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SCALE

	Gloss	1_____3_____5
		less reference more
5		(whole egg)
	Colour	1_____3_____5
		less reference more
		(whole egg)
10	Appearance	1_____3_____5
		worse reference better
		than ref. (whole egg) than ref.
15	Mouthfeel crust	1_____3_____5
		less reference tougher
		tough (whole egg)

TABLE III

Type of glazing agent Sample number	OVEX bakglans	Glazing according to the invention
2 weeks' storage		
6	poor results: very dark surface which showed strange bubbles	poor results: very dark surface which showed strange bubbles
9	smooth surface: light-yellow colouring; good appearance	smooth surface yellow-brown colouring; good appearance
10	smooth surface light-yellow colouring; good appearance	smooth surface light-brown colouring; good appearance

EXAMPLE IV

A pre-mix was made in water of 80°C containing the water, skimmed milk powder and sodium caseinate.

Simultaneously, a mixture of Na-pyrophosphate, unsaturated mono- and diglycerides was dissolved in soybean oil ($N_{20} \approx 0$).

The fat mixture was added to the water phase and the mixture was subjected to Ultra Turrax mixing for 5 minutes. The $D_{3.2}$ (= droplet size) was 3.8 μm .

The composition was sterilized by indirect heat treatment (8 seconds at 140°C).

The composition of the resulting glazing agent was:

	<u>wt%</u>
Water	80.5
Na-caseinate	9.0
SMP	2.0
5 BO	7.94
Emulsifier	0.06
Na-pyrophosphate	0.5

10 The viscosity (η_{20}) of the sterilized product was about 200 mPa.s.

15 An aluminium baking sheet was provided with a thin fatlayer. On this fatlayer a layer of the glazing composition was brought, using a pensil. The system so obtained was heated for 15 min. in an oven at 190°C.

20 Above procedure was repeated using 1) a whole egg glazing composition and 2) a glazing agent as above, but without Na-pyrophosphate.

The baking sheets were cooled for 30 min. after removal from the oven. Cleaning was performed by soaking for 3 min. with water of 55°C.

25 Results:

TABLE IV

	agent	cleaning results
30	whole egg	++
	glazing agent without pyrophosphate	--
	glazing agent with pyrophosphate	++

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CLAIMS

1. Ready-to-use glazing agent comprising a fat-in-water emulsion with the composition :

1-25 wt.% of a liquid vegetable oil;

5-15 wt.% of casein or its salts;

0.005-10 wt.% of an emulsifier, in particular one selected from the group of fatty acid monoglycerides and diglycerides from C₁₄-C₂₂ fatty acids;

0.1-8.0 wt.% of a composition giving a browning upon heating, preferably by a Maillard-type reaction, such as lactose, or a milk product containing lactose;

balance : water.

2. Ready-to-use glazing agent according to Claim 1, wherein 5-15 wt.% of liquid vegetable oil is present.

3. Ready-to-use glazing agent according to claims 1 or 2, wherein the liquid vegetable oil also comprises 2-15 wt% (on oil) of a hydrogenated vegetable fat, in particular hydrogenated palm oil.

4. Ready-to-use glazing agent according to Claim 1, wherein 8-11 wt.% of casein or its salts are present.

5. Ready-to-use glazing agent according to Claim 1, wherein 0.01-1.0 wt.% of emulsifier is present.

6. Ready-to-use glazing agent according to Claim 1, wherein the emulsifier is a mixture of monoglycerides and diglycerides from C₁₆-C₁₈ saturated and/or unsaturated fatty acids.

7. Ready-to-use glazing agent according to Claim 1, wherein 0.3-3 wt.% of lactose or a milk product containing lactose is present.

8. Ready-to-use glazing agent according to Claim 1, wherein the viscosity of the composition at 20°C is 1-10⁵ mPa.s.
9. Ready-to-use glazing agent according to any of Claims 1-8, wherein the glazing agent is sterilized.
10. Ready-to-use glazing agent according to Claim 9, wherein the glazing agent has an ambient shelf-life of more than 3 months.
11. Ready-to-use glazing agent according to Claim 1 or 2, wherein the liquid vegetable oil has a solid fat index at 20°C of at most 7.0.
12. Ready-to-use glazing agent according to Claim 1 or 7, wherein the milk product is skimmed milk powder or buttermilk powder.
13. Ready-to-use glazing agent according to any of Claims 1-12, wherein the droplet size of the emulsion is less than 5.0 µm.
14. Ready-to-use glazing agent according to any of claims 1-13, wherein the glazing agent comprises additionally 0.05-2.5 wt% of a pyrophosphate, in particular 0.1-1.5 wt% of a pyrophosphate of an alkaline metal.
15. Ready-to-use glazing agent according to claims 1-14, wherein the glazing agent also comprises 1-10 wt%, in particular 2-8 wt% of egg-yolk.
16. Deep-frozen, non-baked food products on which a coating layer of a glazing agent is present, wherein the glazing agent has the composition according to any of Claims 1-15.

17. Baked products, including deep-frozen baked, non-frozen baked and gas-packed baked or parbaked food products provided with a coating layer of a glazing agent, wherein the coating is obtained from a composition according to any of Claims 1-15.

18. Use of a glazing agent as a coating layer for baked food products, wherein the glazing agent according to any of Claims 1-15 is applied for the improvement of the gloss, appearance and/or colour of baked, deep-frozen, laminated food products.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 93/01704

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 A21D13/08		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	A21D ; A23G	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	EP,A,0 205 195 (UNILEVER PLC) 17 December 1986 cited in the application see the whole document ---	1-15
Y	US,A,4 389 420 (S.H. YONG ET AL.) 21 June 1983 see claims ---	1-15
A	DE,A,2 303 703 (C.H. BOEHRINGER SOHN) 1 August 1974 ---	
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A	US,A,4 696 826 (S.J. LEUSNER ET AL.) 29 September 1987 see the whole document ---	1-3,14
	--- -/-	
<p>¹⁰ Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
18 OCTOBER 1993		22. 10. 93
International Searching Authority		Signature of Authorized Officer
EUROPEAN PATENT OFFICE		BEVAN S.R.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 93/01704

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	DATABASE WPI Section Ch, Week 7117, Derwent Publications Ltd., London, GB; Class D12, AN 71-28631S & JP,B,46 015 658 (NIPPON CHEMICAL IND. CO. LT.) see abstract -----	1,14
A	FR,A,2 268 476 (HENKEL & CIE G.M.B.H.) 21 November 1975 see claims -----	1,14

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

EP 9301704
SA 76563

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on

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